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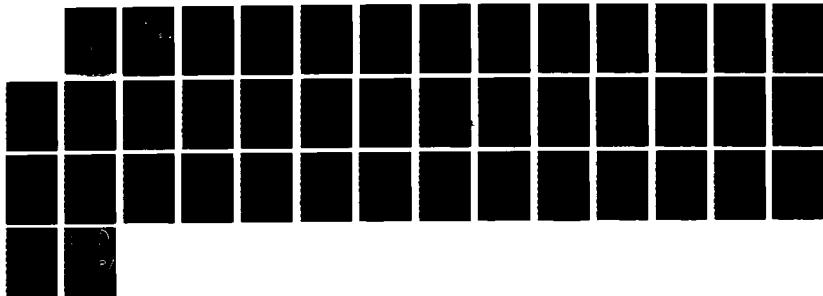
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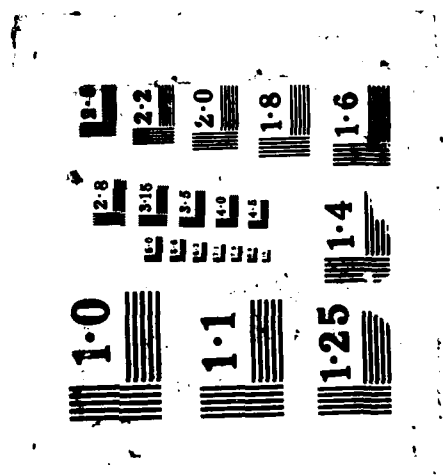
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**CONDUCTIVE POLYMERS
VIA
REACTIVE ALIGOMER**

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, MA 02139

JANUARY 1987

FINAL REPORT
Contract No. N62269-85-C-0297

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FOREWARD

The following report describes work performed on Navy Contract No. N62269-85-C-0297, "Conductive Polymers Via Reactive Oligomers." The work accomplished and reported herein was performed by Massachusetts Institute of Technology, Cambridge, MA. The program was monitored by Dr. Leonard J. Buckley of the Naval Air Development Center, Aerospace Materials Division, Air Vehicle and Crew Systems Technology Department.

INTRODUCTION

Intrinsic conducting polymers as a subfield of polymer science, is now about ten years old. Many gains have been made in the areas of synthesis and mechanism. However it is their poor stability, processability, and mechanical properties which have hindered their infusion into the plastics markets. Although many advances have been made in rendering some of these materials more tractable, they are still short of what is needed for them to be economically competitive with the variety of metal and carbon filled plastics available.

Unlike filled plastics though, conducting polymers can offer unique properties such as high surface area due to extended fibrillar morphology, high charge density, a range of intermediate conductivities, and electrochromism to name only a few. These properties can be developed to meet the needs of specialized applications such as solid state battery devices, electromagnetic shielding, catalyst support, and electrode material. Given that these needs can be met it is still imperative that the processability issue be addressed. Although conducting polymers in many cases can be "blended" with thermoplastics or thermosets allowing them to infiltrate into the filled conductive polymer market, this is not a satisfactory technique for applying them towards the previously mentioned specialty needs.

In this report we will explore some of the basic principles and routes previously taken in pursuing the needed improvements in conductive polymer stability and processability. Our approach has been to derivatize short conjugated segments, which are essentially monomers, of polythiophene

with a short segment of a flexible chain and then polymerize the resulting species into an alternating block copolymer. The underlying belief is that since polythiophenes are known to be fairly stable the block will possess not only this stability but, with the help of the flexible unit, it will possess improved tractability and toughness as well.

CONDUCTING POLYMERS AND STABILITY

A serious problem facing conducting polymers such as $(CH)_x$ is their instability towards ambient O_2 and water either in the pristine state or doped. Stability is an obvious necessity for utilizing these polymers and is partially met with the polyheterocycles such as polypyrrole, PP, and polythiophene, PT. These systems are electron rich in their pristine form resulting in a low oxidation potential (E_{ox} for PP is -0.2 Volts vs. Standard Sodium Calomel Electrode, SSC, and 0.7 Volts vs. Standard Calomel Electrode, SCE(1,2)). Thus, the lower the oxidation potential of the π Lewis base, the more stable the oxidized π Lewis base. PP is oxidatively unstable in its pristine form whereas electrochemically prepared PT and its derivatives can be cycled between the oxidized and reduced form(1,2). PT can be doped with Lewis acids and electron donors although n-type PT is very unstable; attempts to reduce the pristine forms of PP to its anionic state have been unsuccessful.

Figure 1 demonstrates the chemical stability of PP and PT relative to polyacetylene and poly p-phenylene, PPP(1). Note that neutral PP has a

reduction potential lower than O_2 and will be readily oxidized in air.

Oxidized PPP is at a higher potential than water and will be readily reduced in air. PT and $(CH)_x$ have similar redox values; however, $(CH)_x$ is highly susceptible towards O_2 oxidation. It is presumed that the sulfur bridges in PT and resulting aromaticity is responsible for its good stability. Both PT and PP lose only about 20% of their conductivity when stored in air for a year(1,2).

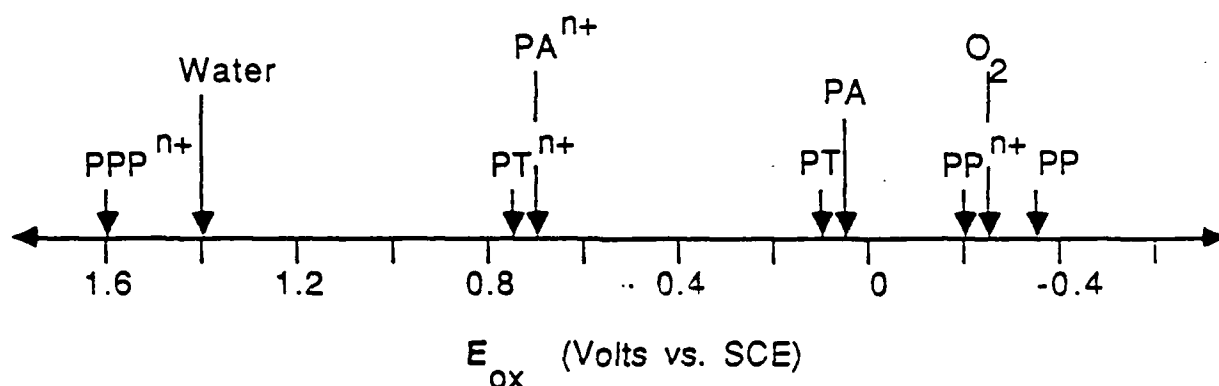
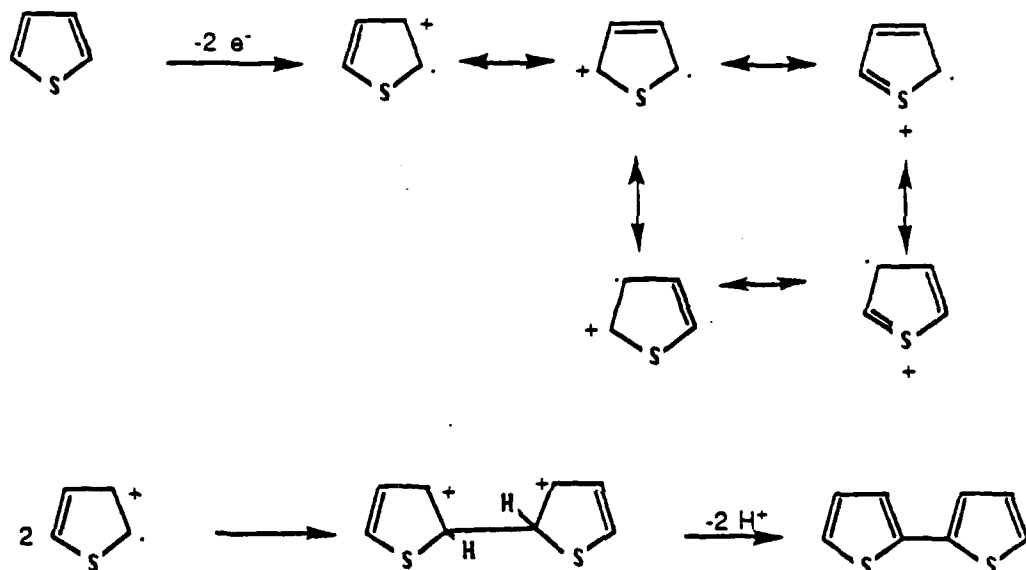


Figure 1.

Thiophene and pyrrole resemble the cyclopentadienyl anion, in that they are aromatic and there is an excess of one π -electron per carbon, although for the heterocycles the majority of the excess π -electron density resides on the heteroatom(3). Pyrrole has an E_{ox} low enough such that it can be polymerized directly under fairly mild conditions ($V_{appl} \sim 0.5$ Volts(2)). PT can be prepared from Ni(II) catalyzed oxidative coupling of the 2-Grignard reagent of 2,5-dihalo thiophene(4). Thiophene can also be electrochemically polymerized to give PT but only at a fairly high potential,

$V_{\text{appl}} > 1.65$ Volts vs. SCE(1). The electrochemical reaction is believed to occur via a pair of single electron transfers from monomers resulting in a pair of radical cations which couple to form the dication. The dication then eliminates two protons generating a dimer which can further chain extend as demonstrated in Scheme 1.



Scheme 1.

The same sort of reaction mechanism is thought to occur in "outer sphere" type chemical redox polymerization of pyrrole, or as we have observed in this laboratory 2,2'-5,2"-terthiophene or α -T₃, with FeCl₃ or AsF₅(5, 6,7). With the five membered ring polyheterocycles, 2.25 to 2.5 electrons per unit are transferred to the oxidant or the anode, two of them associated with oxidative coupling and the remainder is associated with the simultaneous oxidation of the polymer(2).

Note that the above resonance scheme of the radical cation allows

two forms such that coupling is possible at either the α or the β position on the ring. Although α - α' linkages dominate in both PP and PT it is thought that β linkages, as well as cross-links and branching, are the reason behind the lack of crystalline order in the bulk(1). Generally the lowest possible applied potential for polymerization/oxidation is best to thus minimize the concentration of these defects in the polymer, i.e. conditions which give preference to the thermodynamic product not the kinetic product.

Figure 2 demonstrates the inverse relationship between E_{ox} and the number of units for a number of polyarylenes(8). Presumably the more units in the chain, the more delocalized is the radical cation. Thus it has been proposed to prepare PT from thiophene oligomers such as 2,2'-bithiophene ($V_{appl} = 0.7$ Volts vs. Ag/Ag^+) or α - T_3 ($V_{appl} \geq 1.0$ Volts vs. SCE)(9).

"Semi-Crystalline" $P\alpha$ - T_3 has been prepared and is thought to possess an increased degree of order due to the fact that one half of the thienyl linkages start out α - α' in the monomer(10, 11). Depending on the conditions employed, three different forms of $P\alpha$ - T_3 are obtained: a powder and a gel which have moderate conductivities, 10^{-2} S/cm, and possess crystallinity, up to 31%; and a film which is amorphous and has conductivity of 10^{-8} S/cm. Although the initial conductivities are low the gel could be doped with sulfuric acid vapor to a conductivity of 11 S/cm. It has been argued that preparing PT from thienyl oligomers is, in fact, a less effective route since the effective conjugation length is observed to be decreased in the case of $P\alpha$ - T_2 and $P\alpha$ - T_3 (12). The reason for this is claimed to be that the radical cation of the thienyl oligomer is of higher stability such that not

only is the preference for α - α' coupling reduced but more α -T₃⁺ is able to diffuse into solution away from the electrode thereby reducing the yield. Unfortunately the only evidence presented that there is a shorter conjugation length in P α -T₂ and P α -T₃ is the uv-vis spectra of the reduced polymers showing a decrease in the λ_{max} as the number of units in the monomer increases. The data presented do not show the conjugation lengths to be all that different. Ir analysis would be essential to demonstrate the presence of coupling defects. As for the lower conductivity generally observed with the polymerized oligomers compared with polymerized thiophene, it possibly could be that the films or powders are not fully oxidized into the conductivity plateau since the unpolymerized monomer still in solution could partially reduce the polymer(13). This is an interesting aspect which should be further investigated.

With respect to Figure 2 it is important to note that in these systems the E_{ox} reaches a minimum rather quickly so that, for instance, the E_{ox} of PT is close to sexithiophene, α -T₆. The significance of this is that lower molecular weight polymers, or oligomers as the case may be, might be sufficient for high conductivity. Shorter chains could possibly be more tractable and still possess good electrical properties. For α -T₆, as an example, it is not altogether clear that this oligomer is very soluble in organic solvents, but could be of sufficient chain length for high conductivity(14). β -alkyl substitutions on the thienyl chain have been shown to reduce the E_{ox} and enhance the processability of PT(15).

Polythiophene's demonstrated advantage in stability over $(CH)_x$ and PP makes it an attractive component in the block copolymers we propose to prepare. In this work oligothiénylenes will be derivatized to yield a processable prepolymer. The product will then be polymerized into an alternating block copolymer possessing not only the stability of PT but, enhanced physical properties as well.

PROCESSABLE CONDUCTING POLYMERS

Highly conducting polymers all possess the common trait of extended π -conjugation along the backbone. The conjugation is necessary for delocalization, and hence stabilization, of the charge carriers. Unfortunately extended π -conjugation necessitates coplanarity which will result in rigid rod behavior and intractability. In recent years however there have been several approaches towards improving the tractability and hence processability of these polymers. These approaches range from using soluble precursor polymers to manipulating the backbone through copolymerization.

Poly-p-phenylenesulfide (PPS, Ryton) is a soluble engineering thermoplastic which upon doping with AsF_5 vapor is rendered highly conducting although it too becomes intractible and unstable. Both properties are presumably due to the formation of dibenzothiophene units

and intermolecular crosslinking(16). Frommer and colleagues doped PPS with an AsF_3 solution of AsF_5 which simultaneously dissolved and doped the PPS (17). The pristine polymer is not soluble in AsF_3 alone. The resulting blue solution has a conductivity of 0.02 S/cm. From this solution a film can be cast with a conductivity of 200 S/cm. Re-dissolution of this is impossible due to inter- and intrachain crosslinking which occurs once the polymer chains are brought into close contact. The resulting conducting PPS films are homogeneously doped and have marked increase in conductivity; they also exhibit improved mechanical properties over vapor doped PPS. PPS is also doped and subsequently dissolved in a number of superacids which are also strong oxidizing agents such as FSO_3H (18). It seems that for doped PPS to dissolve it must be simultaneously oxidized and solvated. This is supported by the fact that strong acids which are not strong oxidizing agents, like HBr-AlBr_3 , are not successful in doping or dissolving PPS. From this laboratory it has been observed that chemically prepared poly α -terthiophene, $\text{P}\alpha\text{-T}_3$, (i.e. $\alpha\text{-T}_3$ treated with FeCl_3 gives a red solid with conductivity 10^{-3} S/cm) dissolves in chlorosulphonic acid and sulphuric acid yielding a black solution. PP similarly prepared does not, however, dissolve. This disparity could be due to the PP being more extensively oxidized than the $\text{P}\alpha\text{-T}_3$, which is apparent from the latter's red color and low conductivity. $\text{P}\alpha\text{-T}_3$ can therefore undergo solvation/ oxidation in chlorosulphonic acid similar to PPS in say fluorosulphonic acid.

Poly (phtalloyanato siloxane), $[\text{SiO}(\text{Pc})]_n$, is another example of a

processable conductive polymer precursor since it dissolves in concentrated sulphuric acid the solution of which can be spun into fibers. These fibers can be doped with I_2 vapor and have higher conductivities than pressed pellets of $[SiO(Pc)]_n$ due to lower inter-particle resistance of the former(19). The mechanical properties of the $[SiO(Pc)]_n$ in fiber form can be improved by adding KEVLAR™ to the dope and co-spinning a fiber blend. In this case the fiber conductivity increases with the weight fraction of $[SiO(Pc)]_n$.

Blending of two or more polymers is done in order to combine into one the properties of each component. Since the thermodynamic driving force is small for alloying most polymers, not to mention ones which are intractable, the approach for conductive polymers has been to impregnate a processable polymer host with polymerization catalyst, or to coat it onto an electrode, and grow the conducting component *in situ*. In such a fashion polyethylene has been impregnated with $Ti(OBu)_4/TEA$ and exposed to acetylene gas yielding a film which is dopable (σ increases with the weight fraction of $(CH)_x$) and possesses improved mechanical properties and environmental stability(20).

Composites of polypyrrole, (PP), and host polymers such as poly(vinylalcohol), PVOH, and PVC have been prepared. With a technique similar to that used in preparing the $(CH)_x/(CH_2)_x$ composites. PVC has been impregnated with $FeCl_3$ and exposed to an ethereal solution of pyrrole or simply pyrrole vapor(7). The opposite procedure is possible whereby PVC is

impregnated with pyrrole and is exposed to FeCl_3 vapor since FeCl_3 can be sublimed. On the other hand PP has been grown on PVC coated electrodes, as well as a number of other thermoplastics, yielding conducting composites which, in this case, are semitransparent with a conductivity between 2-5 S/cm(21,22,23). Similarly pyrrole and thiophene have been electrochemically polymerized on a Nafion™(polyfluorosulphonate ionomer) impregnated fabric covered electrode resulting in a film with mechanical properties similar to the host and with conductivities between 20-50 S/cm for the PP composites(24). PT/ Poly (THF) composites have been prepared by polymerizing 2,2'-bithiophene onto electrodes previously coated with electrochemically polymerized THF yielding flexible free standing films the conductivity of which is comparable to that of $P\alpha\text{-T}_2$ (25).

Another interesting approach to electrochemically preparing processable PP films is to use a polyelectrolyte counterion(31). Films of this sort which have been prepared are heat processable and flexible but have a lower conductivity, 10^{-3} S/cm.

Alkyl substituted monomers have been homopolymerized and copolymerized with unsubstituted monomers with the hope that the alkyl group directly bonded to the backbone will improve the tractability. Polymerization of α -alkynes has yielded, for example, poly (methyl acetylene) which is soluble but is less stable in air than $(\text{CH})_x$ and is poorly conducting(26). Apparently the alkyl group sterically hinders the backbone from coplanarity resulting in poor π -overlap. Copolymers of acetylene and α -alkynes are similarly less stable than homopolymers of acetylene and

conductivity is again lower and varies as a function of the fraction of $(CH)_x$. However, contrary to the problems associated with substituted $(CH)_x$, poly(3-alkyl and alkoxythiophenes) have been prepared chemically and electrochemically yielding polymers with superior properties to simple PT. The advantages of these substituted thiophenes is that the lower E_{ox} , due to the electron donating capabilities of alkyl and alkoxy groups, enables one to employ mild polymerization conditions, i.e. a lower applied potential, and results in a more stable conducting polymer. Poly(3-methoxythiophene), PMeOT, is reported to be soluble and more stable than PT, and poly(3-methoxy-2,2'-bithiophene) is more stable than PMeOT(27,28). Similarly, poly(3-methyl, ethyl, butyl, and thiomethylthiophenes), chemically prepared via the coupling of the α -Grignard reagent of the 2,5-dibromo-3-substituted thiophene, have high conductivities (ca. 10^0 S/cm). These polymers also exhibit increased stability and solubility, in organic solvents such as chloroform, in the sequence n-butyl > ethyl > methyl (15).

A copolymer of pyrrole and phenol has been prepared electrochemically and is reported to have improved flexibility while retaining good conductivity, 4 S/cm(29). The dopants or electrolytes used in this study, BF_4^- and ClO_4^- , generally result in brittle films of homo-PP(30).

A more successful approach with polyacetylene has been to graft it onto polybutadiene (PBD) and polystyrene (PS) with a small fraction of copolymerized butadiene units, that have been selectively epoxidized with O_2 or m-chloroperbenzoic acid(32). Active $(CH)_x-TiR_3$ attacks at the epoxy

units on the PBD or PS dissolved in the Shirakawa catalyst solution. The result is that the flexible portion of the graft pulls the inflexible $(\text{CH})_x$ chain into solution, in a solvent such as chloroform, from which films can be cast.

An alternative approach to preparing grafts has been to expose n-doped $(\text{CH})_x$ to such monomers as ethylene oxide, MMA, styrene, and isoprene in order to initiate the anionic polymerization of these monomers(33). The result is a soluble shell around the $(\text{CH})_x$ backbone which helps solubilize the backbone but may have caused, due to an insulating effect, the lower conductivities observed. Recently a similar approach has been to substitute alkyl halides, such as pentyl bromide, with the nucleophilic centers of n-type $(\text{CH})_x$ to yield a swellable and rubbery copolymer which can be doped to a highly conductive state, but becomes very brittle(34).

Through an anionic-to -Ziegler-Natta transformation polymerization technique, block copolymers of styrene and $(\text{CH})_x$ have been prepared(35). In this reaction the "living" polystyryl anion reduces $\text{Ti}(\text{OBu})_4$ to the active catalyst which is subsequently exposed to acetylene gas. Two fractions are observed, one is soluble but of low conductivity, while the other is insoluble and has a higher conductivity.

With the last approach in mind, we have attempted to prepare block copolymers of thiophene or pyrrole and a flexible unit. It is hoped that the flexible unit will increase the solubility of the polyheterocycle and improve its bulk mechanical flexibility as well. Namely through a choice of several

chemical routes, to be discussed below, we proposed to prepare a fully soluble polymer precursor which could be polymerized into an ABA or $(AB)_x$ type block copolymer, where A represents the inflexible conductive segment and B represents a flexible spacer.

SYNTHESIS

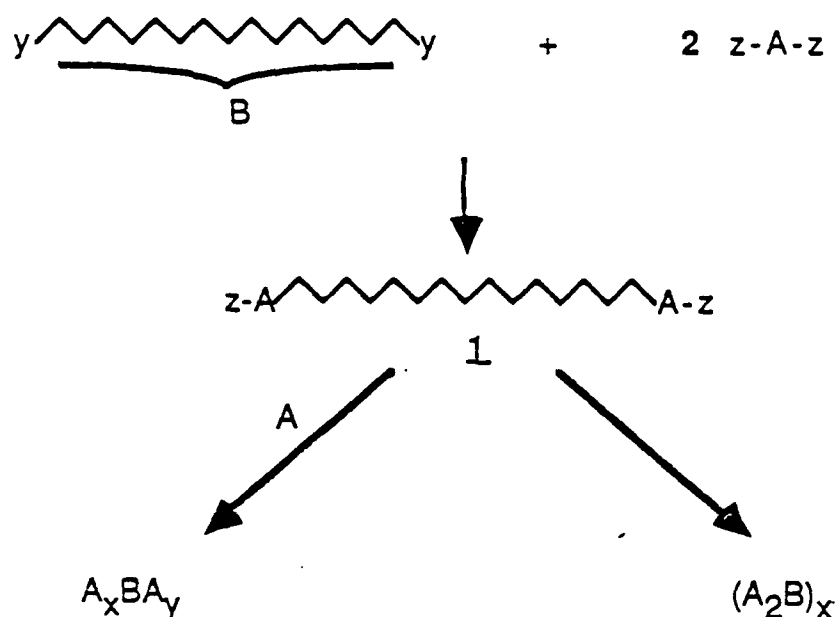
1. Introduction

The proposed structural modification was aimed at rendering PP and PT processable without reducing the bulk conductivity and, if possible, to concomitantly improve the toughness of these materials, Scheme 2. To achieve this goal we prepared a telechelic precursor polymer of intermediate molecular weight and completely processable. Depending on the nature of the endgroup functionality, the prepolymer can either serve as an "initiator" site for an ABA triblock copolymer, when reacted with A monomer, or it can be homopolymerized into an $(AB)_x$ block copolymer if the A_2 dimer is of suitable length for high conductivity, Scheme 1.

2. Oligomer Derivatization

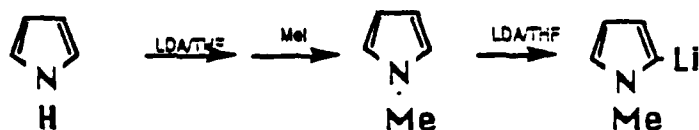
There are several routes accessible in preparing oligothiényl derivatives of 1. Although α - T_3 is not commercially available it is easily

prepared from the Ni(II) coupling of the 2-thienyl Grignard reagent and 2,5-dibromothiophene(36). α -Terthienyl carboxylic acid, α -T₃COOH, can be easily prepared and derivatized to the acid chloride which can then be used to endcap α,ω -dihydroxy endcapped flexible chains such as polyethylene glycols, PEG, which are commercially available in various molecular weights. Pi-excessive heterocycles offer unique advantages over rings such



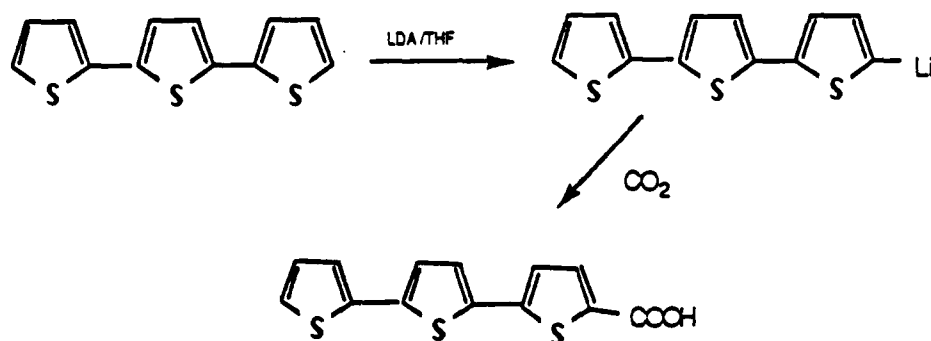
Scheme 2.

as benzene due to their higher reactivity. Thiophene is easily lithiated in the α position while the 1 position of pyrrole must be protected in order to lithiate the ring:

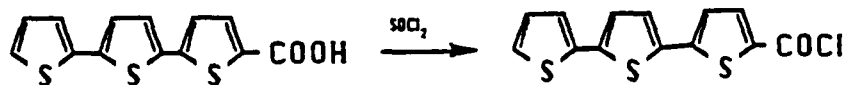


α -Terthienyl lithium, α -T₃Li, is then treated with solid CO₂ to give

α -T₃COOH:



Apparently the 5" carbon in α -T₃ is not significantly affected by the carbanion at the 5' position such that in a 1:1 ratio mixture of LDA, or BuLi, to α -T₃ an equilibrium exists between the 5',5"-dianion, the 5'-anion and neutral α -T₃(37). Thus a 100% excess of α -T₃ must be added to any lithiation reactions. Treating α -T₃COOH with a large excess of SOCl₂ will give the acid chloride, α -T₃COCl:



Initial results of this synthesis have given an orange solid (recrystallized from benzene) with an MP of about 130° C. Mass spectrometry gives a parent ion at 310 and a fragmentation pattern consistent with that expected for

α -T₃COCl(38). Elemental analysis however shows that some hydrolysis occurred prior to analysis.

3. Prepolymer Preparation

i. Di-esters

An excess of α -T₃COCl (at least 25%) is reacted with PEG, molecular weight 400 (GPC in DMF gives an M_n of 440), in the presence of a base such as triethylamine. To remove the excess acid chloride, the product mixture is purified by running the reaction residue through an alumina column and collecting the appropriate fractions. Proton nmr is used to evaluate the extent of the reaction by comparing the peak integration at about 7 δ , corresponding to the α -T₃ protons, to that at about 4.2 δ , corresponding to the methylenes α to the ester, and the broad peak at about 3.4 δ due to the rest of the protons in the PEG chain(39). We have not been successful in achieving complete conversion of the PEG hydroxyls.

Because α -T₃ derivatives are not exceedingly soluble in organic solvents such as toluene, which was the solvent initially used in this reaction, it is thought that this lack of solubility, particularly the active α -T₃CO⁺(Et₃N:Cl)⁻ acylating species, is preventing complete conversion. Winnik *et. al.* however, have prepared similar compounds, with complete conversion of the hydroxyl moiety, from a PEG and 2-pyrenyl butyryl chloride (40). However in this synthesis, the acid species was an aliphatic

acid chloride which is considerably more reactive than an aromatic acid chloride used in our prep since the latter is resonance stabilized(41). In fact initial endcapping esterifications, in this study, with acetyl chloride and PEG-400 yielded complete conversion. On the other hand similar reactions with the same PEG and benzoyl and thienoyl chloride, both with high solubility in toluene, did not consistently give complete conversion of the hydroxyls.

The proposed solution to this problem is to react α -T₃COOH and PEG in the presence of the strong nucleophilic catalyst 4-dimethylaminopyridine, DMAP, and use dicyclohexylcarbodiimide, DCC, to trap the water condensate forming dicyclohexylurea(42). DMAP forms an activated complex with the acid group increasing its accessibility to the hindered hydroxyl group. **Scheme 3(43).** The use of this catalyst can increase the reaction rate three orders of magnitude over reactions catalyzed with TEA or pyridine. Furthermore the nucleophilic catalyst may eliminate the extra step involved in synthesizing the acid chloride of α -T₃COOH. However we have not been able to try this reaction.

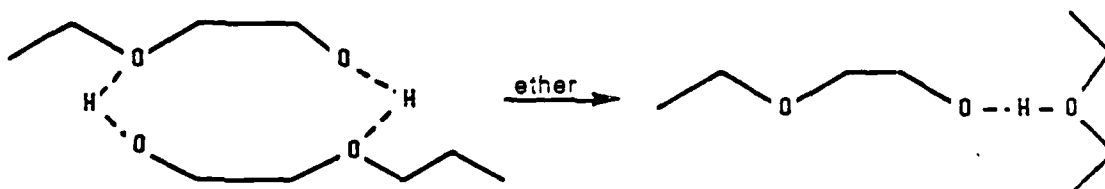
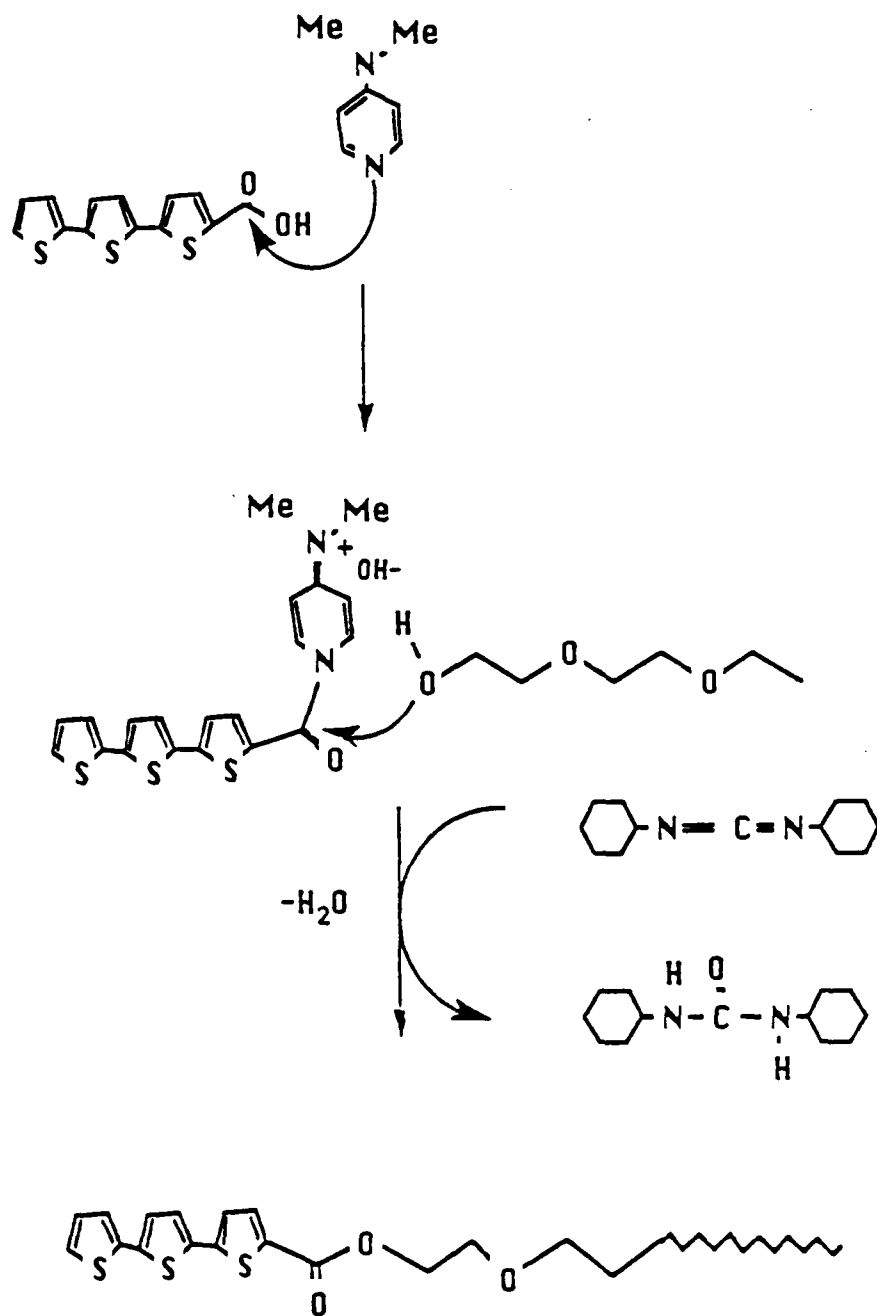


Figure 3. Deactivating intra and inter-molecular H-bonding in PEGs can be reduced by using an H-bonding solvent such as ethly ether.

It is known that the presence of internal ether oxygens influences the

reactivity of the terminal hydroxyls(44). The inductive effect of adjacent ether linkages will diminish the basicity while inter and intramolecular H-bonding can hinder the end hydroxyl towards the acid. Switching from toluene to a solvent capable of H-bonding with the end group will eliminate the latter effect in addition to possibly activating it, Figure 3. Furthermore the choice of TEA, or perhaps even pyridine, was not optimal since once the activated acylium complex is formed it can precipitate from the reaction mixture. Tributyl amine might have been a better choice of bases because it forms a more soluble active complex(44).

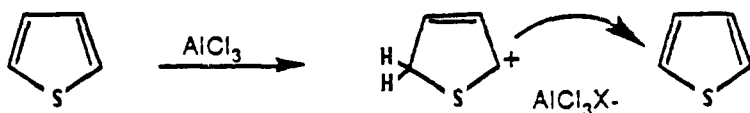


Scheme 3.

ii. Diketones

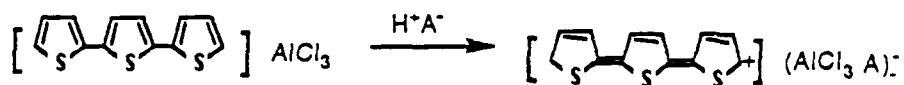
An alternative approach is to treat two equivalents of α -T₃Li with an α,ω -dihalo alkane; however this method suffers from the lack of commercially available α,ω -dihalo alkanes. A similar product is obtained by acylating two equivalents of α -T₃ with one equivalent of a diacid chloride like sebacoyl chloride. Once this has been accomplished it can presumably be extended to longer diacids, which are commercially available, that are converted to the corresponding acid chloride upon treatment with SOCl₂ and a drop of DMF(45).

There are a number of catalysts available for acylating thiophenes, which occurs almost exclusively at the α position(46,47). Pi-excessive aromatics such as thiophene and pyrrole are relatively stronger carbon Bronsted acids than benzene such that AlCl₃, which is the most common acylating catalyst, will initiate cationic polymerization of the ring(47):



Thiophene can be easily acylated with acetyl chloride in benzene using SnCl₄ as the catalyst(48). Previous acylations of α -T₃ have only employed

weakly oxidizing catalysts such as phosphoric acid with acid anhydrides(49). Therefore we have qualitatively evaluated the efficiency of some Lewis acids, listed in decreasing order of acylating activity, $\text{SnCl}_4 > \text{TiCl}_4 > \text{ZnCl}_2 > \text{BF}_3 \cdot \text{OEt}_2$ in synthesizing the ketone $\alpha\text{-T}_3\text{Ac}$ (47). In all cases it appears that $\alpha\text{-T}_3$ and the catalyst form a charge transfer complex by inference from the dark purple color formed upon mixing. Presumably this color is due to the existence of **2** which can be hydrolyzed upon addition of water giving back $\alpha\text{-T}_3$ (47,50). This appears to be the case with $\alpha\text{-T}_2$ as well(50).

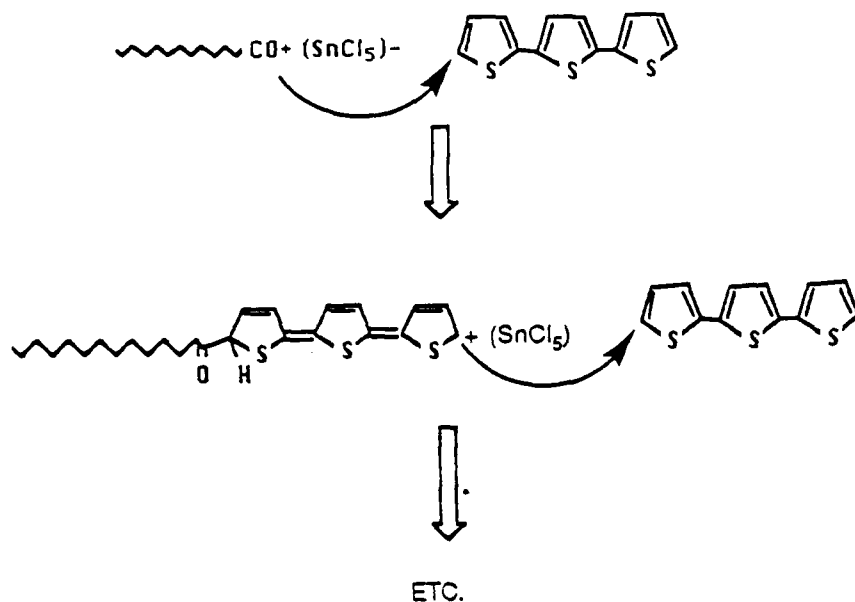


2

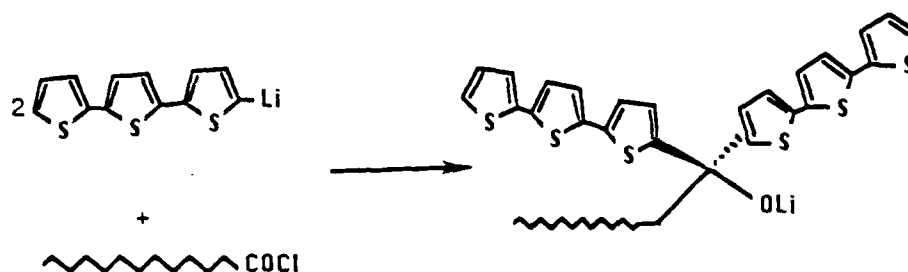
However only SnCl_4 and TiCl_4 were successful in producing the desired ketone.

Sebacoyl chloride treated with an excess of thiophene in the presence of SnCl_4 gives essentially pure bis-(2-thienyl)-sebacyl ketone, TTSK. This is determined from comparing the peak integrations on the proton nmr spectrum; ir analysis shows that the carbonyl peak has shifted to the lower energy (lower wavenumber) associated with the transition from an acid, ca. 1760cm^{-1} , to a ketone, ca. 1680cm^{-1} (39). However when this procedure was used to prepare the corresponding bis[2-($\alpha\text{-T}_3$)]-sebacyl ketone, $\alpha\text{-T}_3\text{SK}$, the reaction workup gave an insoluble red/brown precipitate and

α -T₃ which was presumably the excess. In analysis of the insoluble fraction showed the presence of both ketonic and acidic carbonyls, aliphatic and aromatic C-H's, and some acidic hydroxyls. One possibility is that once the acylation reaction occurred, subsequent cationic oligomerization took place:



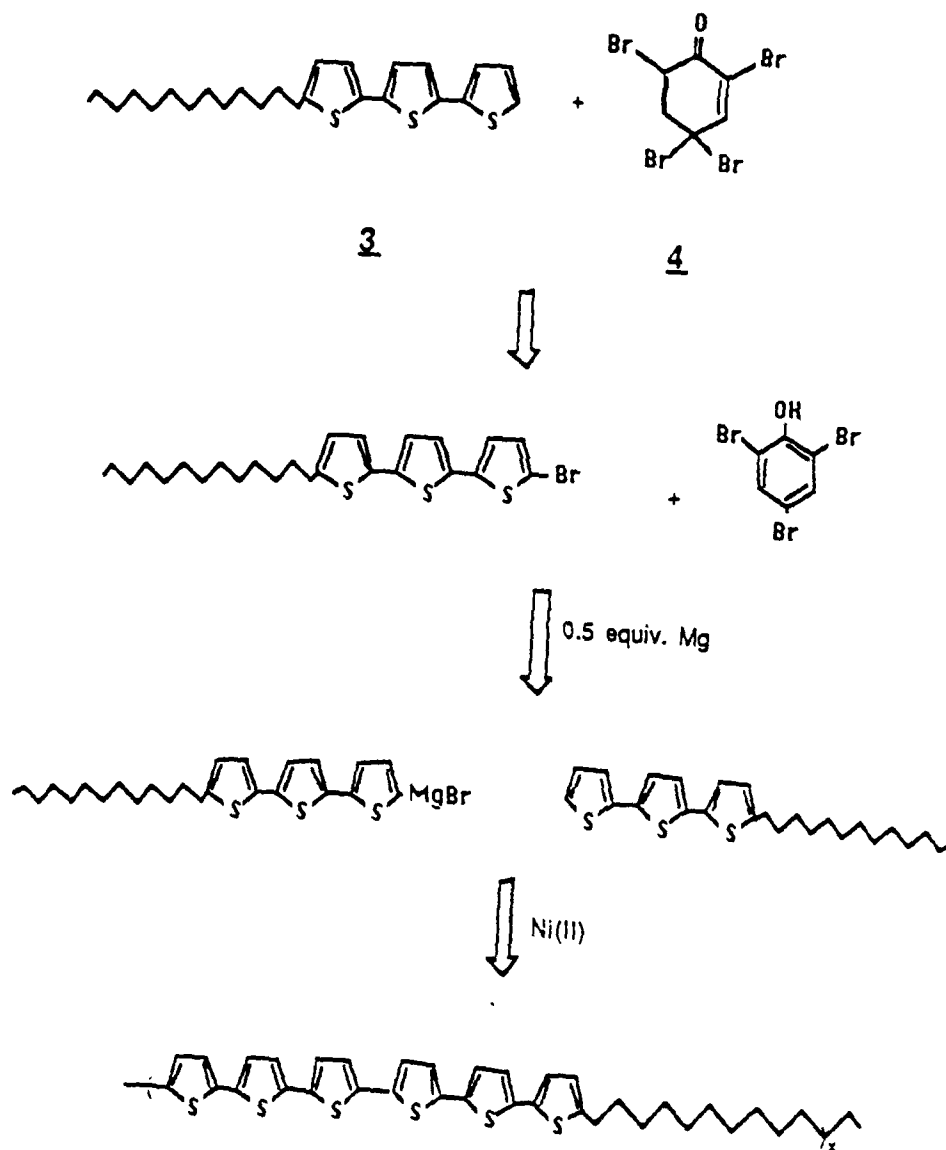
To prevent this coupling reaction from occurring it might be possible to use the weaker Lewis acid TiCl_4 . If this is not possible, a less efficient means of preparing the ketone is to treat two equivalents of α -T₃Li with a single equivalent of diacid chloride. This reaction is less attractive both due to α -T₃ anion: dianion equilibrium described above and also because a second α -T₃Li can attack the carbonyl giving the corresponding alcohol:



Therefore the reaction must be done at -78°C without an excess of carbanion.

4. Block Copolymer Synthesis

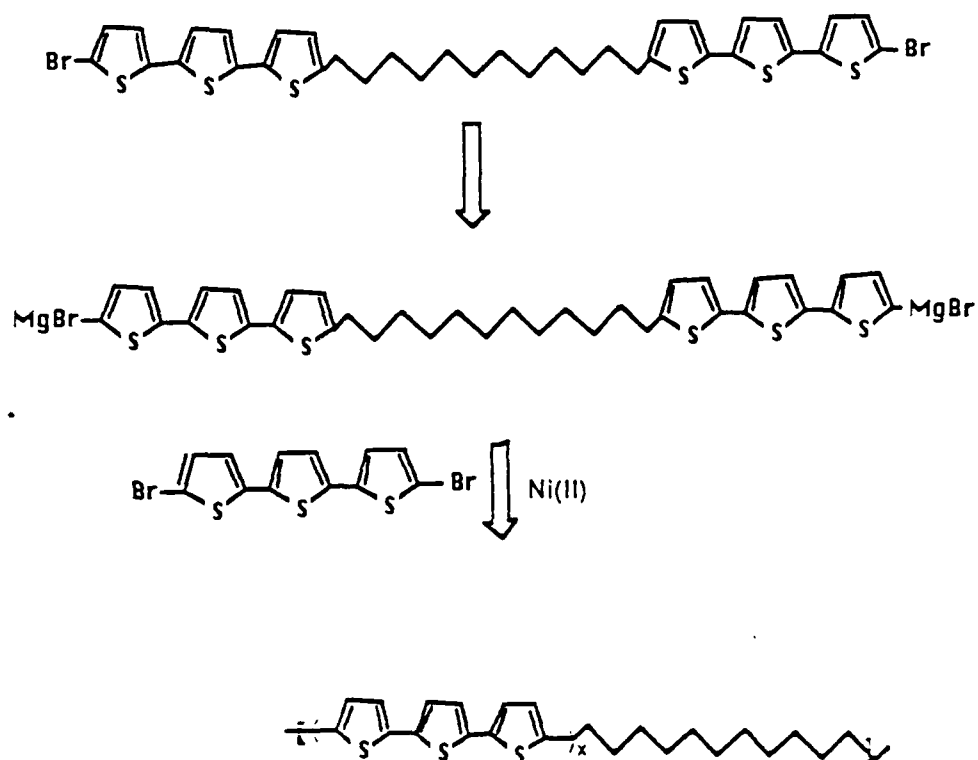
Coupling of the $\alpha\text{-T}_3$ endgroups to give $(\text{AB})_x$ can be done in a random fashion with an oxidizing agent like FeCl_3 recognizing the likelihood that the less desirable $\alpha\text{-}\beta'$ or $\beta\text{-}\beta'$ coupling is possible. The other alternative is to selectively brominate the $\alpha\text{-T}_3$ endgroup at the α'' position with either N-bromosuccinimide or 2,4,4,6-tetrabromo-2,5-cyclohexadienone, treat with 0.5 equivalents of Mg metal, and polymerize the system by oxidative coupling with a Ni(II) catalyst(12), Scheme 4.



Scheme 4.

This method is clearly a more synthetically involved approach, but one which offers the advantage of controlled α - α' placement of the α -T₃ units

with the additional advantage being that the aromatic "block" can be controllably lengthened by the addition of the terminal Grignard reagent of α -T₃SK to an ethereal solution containing 5',5"-dibromo- α -T₃ and a Ni(II) catalyst, **Scheme 5**.



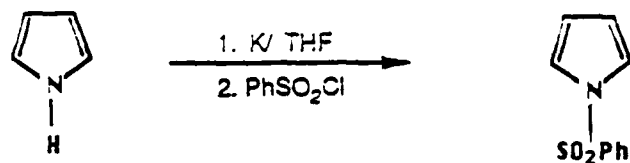
Scheme 5.

5. Alternatives

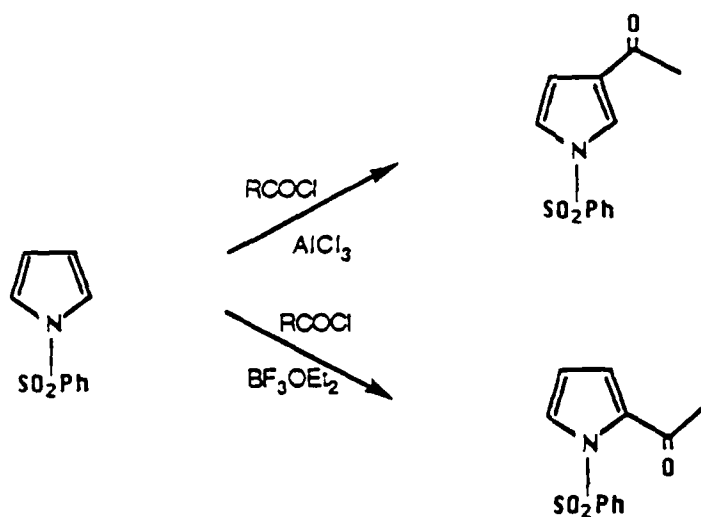
An alternative route is to polymerize thiophene, or even better 3-methylthiophene, in the presence of the prepolymer. In this way an ABA type block copolymer can be obtained. There is no guarantee however, that the prepolymer will be covalently incorporated into the system and that the thiophene will not simply form homopolymer. Homopolymer will invariably contaminate the product and complicate the characterization. The E_{ox} of the prepolymer will need to be matched with that of the monomer. This can be accomplished by choosing the appropriate oligothieryl group. For example, reduction of the carbonyl groups in TTSK to methylenes with ethanolic $NaBH_4$ might enable the synthesis of ABA blocks if the E_{ox} of the resulting material is close to that of 3-methylthiophene (51). This is probably not an optimal approach since the likely product will be a "blend" of sorts, comprised of triblock and homo-PT.

It is apparent that the chemistry covered above is not necessarily restricted to thiophenes. Acylation of pyrrole, for instance, is not as simple because the ring is much more reactive than thiophene and is subsequently N-acylated along with multiple positions on the ring(46,47). Pyrrole can easily be derivatized with $PhSO_2Cl$ at the 1 position to give N-

$PhSO_2$ pyrrole(52):



This group sufficiently reduces the electron density in the ring such that it can be selectively acylated(53):



Presumably the same sort of chemistry can be applied in the preparation of a prepolymer. Once obtained the the PhSO_2 group is removed via alkaline hydrolysis, and the prepolymer can be treated like the oligothieryl derivative discussed previously.

SUMMARY AND CONCLUSION

The project began by attempting to synthesize a flexible backbone polymer with conjugated electroactive pendant groups. However due to the size of the group that is necessary for high conductivity to occur, the

pendant groups would have to be dimerized leading to a intractable material.

Therefore we have directed our attention towards linear polymers with conjugated and flexible blocks alternating along the backbone. This way longer chain blocks can be directly incorporated into the polymer without crosslinking, thus retaining processability. Possibly the conjugated blocks will have a better chance at forming extended phases than when attached to the backbone as a pendant group.

Our attempts at encapping PEG-400 with α -T₃COCl have resulted in prepolymer with monocapped impurity which we have been unsuccessful in separating out. Acylating α -T₃ with sebacyl chloride is another route towards these polymers which is extremely simple with thiophene but has yielded an insoluble product with α -T₃. Unfortunately these encapping reactions have various complicating factors which must be worked out before polymerization-quality prepolymer can be obtained in good yield. High quality prepolymer is essential for the proposed polymerization route but it is felt that the specificity the Grignard reagent-halide coupling reaction provides is crucial in preparing conductive block copolymers.

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